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(54) Title: METHOD OF CREATING A STONEWASHED APPEARANCE IN WET-PROCESSED FABRICS (57) Abstract <p>A method of treating dyed cellulosic fabric to create a stonewashed appearance by contacting the fabric with a water-based composition having an acidic pH and including at least one cellulase enzyme having optimum activity in an acidic medium and a dye redeposition inhibiting additive selected from the group consisting of natural and synthetic inorganic silicates, polyalkylene oxide polymers, acrylic polymers, and natural, synthetic and semisynthetic polysaccharides. The fabric is preferably indigo-dyed and may be in unsewn form or in the form of a garment or other article composed of sewn fabric.</p>		

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METHOD OF CREATING A STONEWASHED APPEARANCE IN WET-PROCESSED FABRICS.

The invention relates to methods for producing a stonewashed effect in fabrics and garments while reducing redeposition of dye on the treated materials.

Wet-processing of fabrics and garments to produce a variety of visual effects enhancing the appeal of the treated materials is a well known practice. This practice is particularly popular when the garments are indigo dyed and/or the garments are constructed from denim fabric, as with jeans, jackets, skirts, etc., as well as certain accessories and various non-garment items similarly constructed.

Of the more popular wet-processing procedures, abrasion of indigo dyed garments or "stonewashing" has become commercially widespread. For purposes of clarity, and to be consistent with industry terminology, "stonewashing" is considered a process whereby color is removed from a cellulosic garment or fabric by the mechanical abrasion of pumice stones or other abrasive materials, usually in a water bath in a tumbler or washer, such that localized abrasion creates lighter spots or areas on the surface of said fabric or garment leaving a relatively untouched background. Further, processes which produce a similar appearance to said abraded fabric or garments by chemical or enzymatic means, or combinations of the above with or without mechanical abrasion, are included in the definition of stonewashing as it is accepted in the industry.

The most common class of enzyme used to impart the modified appearance is cellulase. Cellulase enzymes are

typically divided into two groups: those with greatest activity at a neutral pH range (pH about 6 to 8), and those with greatest activity in the acid pH range (pH about 4 to 6). These ranges represent the pH values of optimum performance, even though each type of enzyme has some activity outside its stated pH range. Both types are commonly used to impart the "stonewashed" appearance and both have advantages and disadvantages.

One of the advantages of the neutral cellulase treatments is that only a moderate amount of indigo dye removed during the washing process is redeposited onto the white portions of the fabric, thus producing stonewashed denim garments that have bright, clean appearing highlighted areas. The major disadvantage is that, typically, a neutral cellulase enzyme will react somewhat slower than an acid cellulase enzyme, thus lengthening processing times.

A major advantage of the acid cellulase treatments is that the reaction on fabric is much faster than a neutral cellulase enzyme. A reaction time of two to five times faster than a similar treatment with a neutral cellulase enzyme is not uncommon. The major disadvantage is that a greater amount of dye is redeposited onto the garments due in part to the lower solubility of indigo at the lower pH.

Methods and compositions for chemically stonewashing fabrics or garments generally are set forth in, for example, U.S. Patent Nos. 4,832,864, 4,912,056, 5,006,126 and 5,122,159. Improved compositions and techniques are required, however, for processing dyed material with fast-acting acid cellulase enzyme treatments while reducing the quantity of redeposited dye, thus

rapidly yielding garments with areas of bright, clean contrast and an attractive stonewashed appearance.

It is the object of the present invention to provide a method of wet-processing dyed cellulosic fabrics and garments to chemically create a stonewashed appearance in a rapid and effective manner.

It is a further object of the present invention to provide a method as aforesaid which yields fabrics and garments having bright and clean appearing highlighted areas of color variation where dye has been removed.

It is yet a further object of the present invention to provide a method as aforesaid wherein fast-acting acid cellulase enzymes can be utilized as the principal dye-removing agents and yet redeposition of dye on the treated material is substantially avoided.

Still another object of the present invention is to provide a method as aforesaid which is particularly well-adapted for processing indigo dyed denim fabrics or garments.

In keeping with these objects and others which will become apparent hereinafter, the present invention resides in an improved method for treating dyed fabric, either in unsewn form or in the form of a garment, to produce a stonewashed effect by treating said fabric with a water-based composition having an acidic pH and including at least one acid cellulase enzyme and a dye redeposition inhibiting additive selected from the group consisting of natural and synthetic inorganic silicates, polyalkylene oxide polymers, acrylic polymers (homopolymers and copolymers) and natural, synthetic and semisynthetic

polysaccharides, including natural and synthetic gums. The novel method utilizing the foregoing additives enables the use of fast-acting acid cellulase enzymes to remove dye and cause the desired localized variations in color density while substantially preventing "backstaining", the redeposition of dye (particularly indigo dye) from the low pH wash water onto the treated fabric.

The improved wet-processing method of the invention involves contacting dyed cellulosic fabrics, principally cotton denim fabrics, with an aqueous or water-based solution containing (a) a cellulase enzyme having greatest activity in the acid pH range, and (b) a dye redeposition inhibiting additive, as well as optionally other conventional additives such as buffers, surfactants, enzyme activators, solubilizing agents and the like. The fabric is tumbled or agitated together with the aqueous solution.

The fabric treated in accordance with the invention may be in unsewn form or sewn in the form of a garment or other article composed of sewn fabric, preferably a new (unworn) garment or article

The term "stonewashed appearance" as used herein refers to an appearance including local areas of variation in color density on the surface of dyed cellulosic fabrics, resembling the appearance created by mechanical abrasion of the fabric with pumice or other "stones".

Stonewashing is normally carried out in commercial washing machines, cylindrical tumblers, converted dryers or similar pieces of equipment. The necessary parameters for practice of the subject method are that there must be a means to

contain the wash liquor during the process, along with the garments, fabric, or items being stonewashed, such that they and the enzymes and other processing chemicals can make constant or intermittent contact. Further, there must be a means of introducing mechanical energy into the system, allowing the surfaces of the items to be stonewashed to rub against other surfaces, including other fabrics or items being stonewashed. This, in the case of a washing machine or tumbler, is accomplished by rotating the cylinder containing the garments, etc. at such a speed as to allow the garments to move about inside and rub against each other. In the case of a paddle dye machine, this is accomplished by an external paddle wheel mounted at or near the surface of the process liquor. The paddle turns and creates a circulating current. The current and/or the paddle catches the garments and forces them along in such a way as to rub over other garments and the paddle, creating the necessary mechanical action on the goods.

The stonewash process typically consists of several *steps, rather than a single exposure to cellulase enzyme and/or pumice stones. The garments are first typically desized using (a) amylase enzymes and surfactants, (b) oxidizers, alkalis, and surfactants, (c) solvents and surfactants or (d) hot water. This is frequently, but not necessarily, followed by one or more rinses. The abrasion step normally follows, where the cellulase enzyme and other auxiliary chemicals are used to create the abraded appearance. This is the step during which the dye redeposition preventing additives would normally be present according to the invention. Following abrasion there is

sometimes a bleach step (only if the overall color is to be lightened), an antichlor step (only if a bleach step is used), a clean-up step where detergents and brighteners are frequently added to wash away excess loose dye, one or more rinses, and a final softener application. Subsequently, the garments are extracted to remove excess water, then dried and pressed. Although the preferred point to introduce the additives to prevent dye redeposition is with the cellulase enzyme, the additives may provide some benefit if added to the desize operation, the rinses before or after the abrasion, in the clean-up step, or in multiple steps.

While indigo dye is by far the most common dye used on stonewashed fabrics and garments, the stonewash concept applies to any fabric, garment, or article which is made from cellulosic fibers, yarns, or threads, in whole or in part, and is dyed, pigmented, or otherwise colored in such a way as to have a differential of color between the surface and the center of said fibers, threads or yarns, whether the colorant is a vat dye (such as indigo), a pigment (or pigment dye), a sulfur dye, or another classification of dyestuff. The key concept is that the fibers or yarns are "ring dyed", named for the resulting appearance of a cross-section of the dyed fiber, being more heavily dyed on the outermost ring of the fiber, less heavily dyed (or not dyed at all) at the center core. The stonewashing process damages the outermost portion of the cellulosic fibers, exposing the undyed (or lighter-dyed) centers of the fibers.

The dye redeposition or backstaining preventing additives to be used in the novel methods are selected from the group consisting of natural and synthetic inorganic silicates,

such as zeolites, kaolin and bentonite clays; polyalkylene oxide polymers, including polyalkylene oxide polyamine copolymers; acrylic homopolymers and copolymers; and natural, synthetic and semisynthetic polysaccharides, such as natural and synthetic gums and cellulosic polymers.

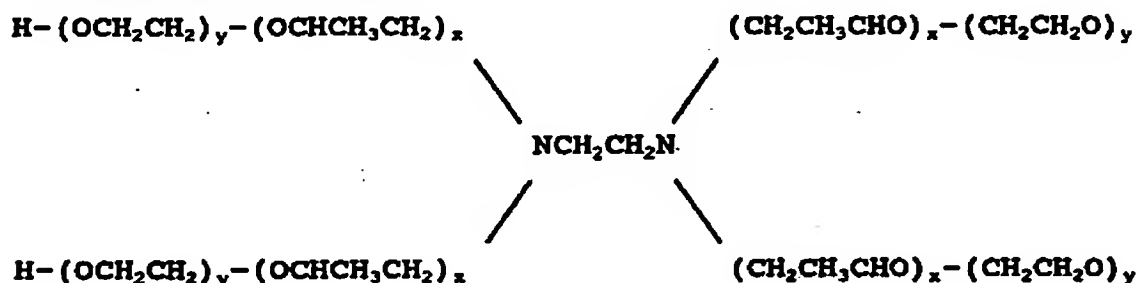
Representative generic structures for several categories of dye redeposition preventing additives to be used in the methods of the invention include but are not limited to, the following:

Natural/Synthetic Inorganic Silicates



Polyalkyleneoxide Polymers

Polyaminoethoxylates

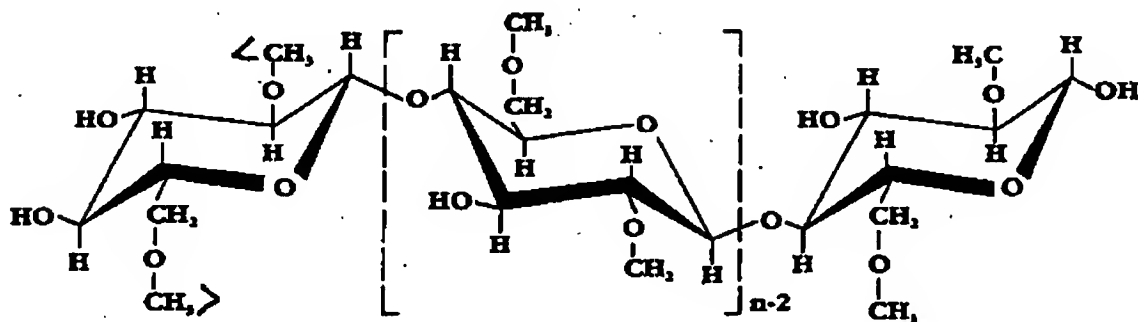
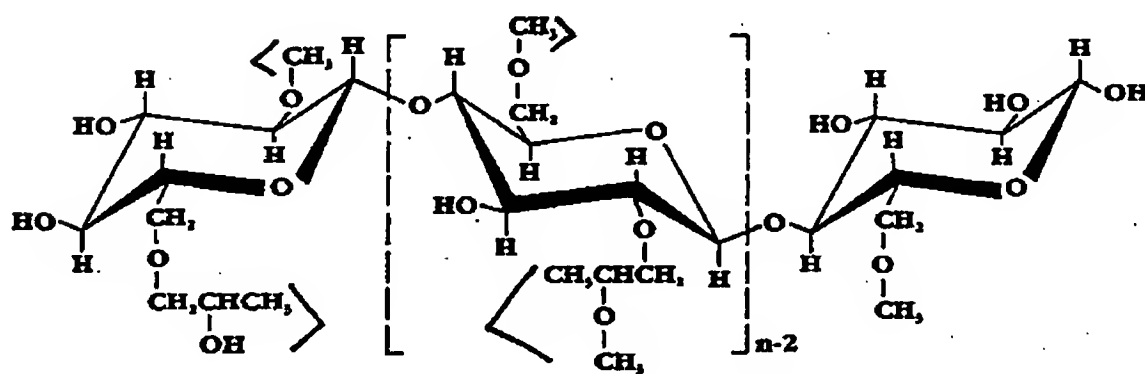


Polyethylene Oxide Polymers

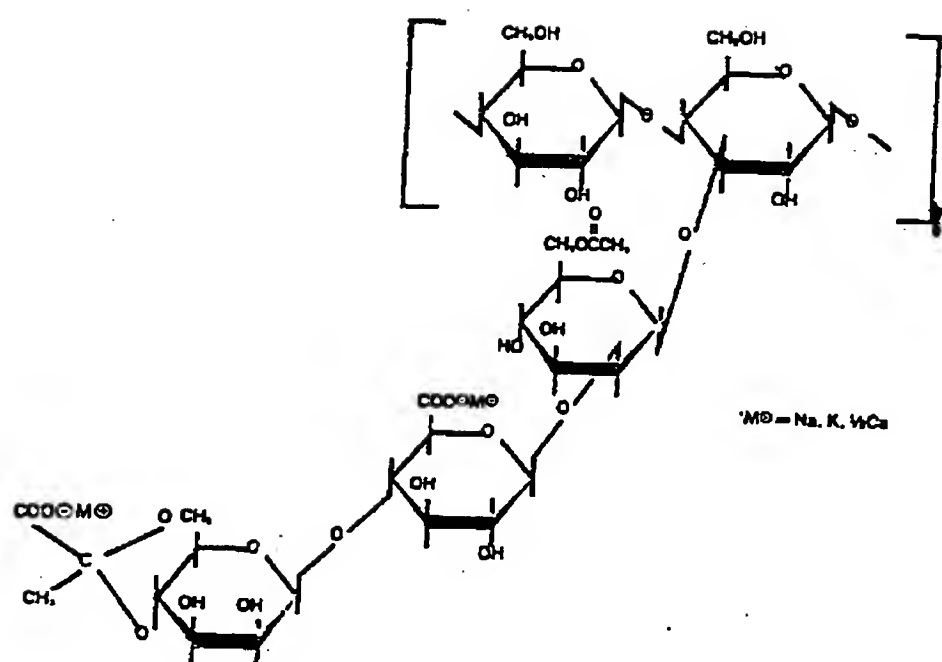


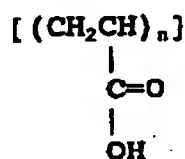
Polyethylene Glycol Polymers



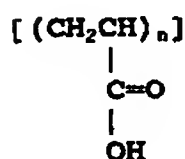
Polysaccharide PolymersMethylcelluloseHydroxypropylmethylcellulose

Xanthan Gum

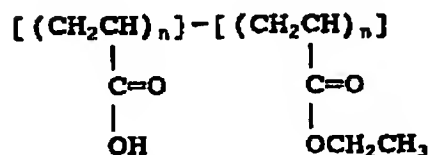


Acrylic Homopolymers and Copolymers

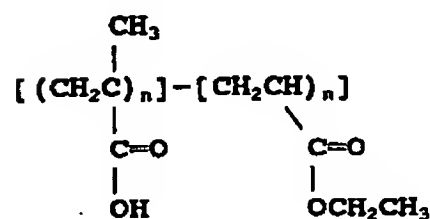
where molecular weight
is $\geq 50,000$.



crosslinked w/polyalkenyl-
polyether where molecular
weight is $\geq 50,000$.



where the ratios of ethyl
acrylate to acrylic acid are
variable and having a
molecular weight $\geq 50,000$.



where the ratios of ethyl
acrylate and methacrylic acid
are variable and molecular
weight $\geq 50,000$.

The following are illustrative examples of compounds or materials identified by brand name, supplier and/or chemical name or structure, which have been found effective as additives to stonewashing solutions in preventing the redeposition even of dyes, such as indigo, which are poorly soluble in acidic solutions:

Product NamesStructural InformationNatural and Semisynthetic
Polysaccharides

KELZAN™
(Merck & Co., Rahway, N.J.)

Xanthan gum

Rhamsan gum

Welan gum

Guar gum

Locust Bean gum

(principally, galactomannan)

KELGIN™ MV, KELGIN™ LV
(Merck & Co.)

Sodium Alginate

Other alginic acid metal salts

KELACID™
(Merck & Co.)

Alginic acid (polymannuronic
acid + polyguluronic acid)

NATROSOL™ 250 HR
(Aqualon Co., Wilmington, DE)

Hydroxyethylcellulose

METHOCEL™ E5, E4M
(The Dow Chemical Co.,
Midland, MI)

Hydroxypropylmethylcellulose

METHOCEL™ HB-100
(The Dow Chemical Co.)

Hydroxybutylmethylcellulose

Gelatin

Casein

Natural/Synthetic Inorganic Silicates

Kaolin

$H_2Al_2Si_2O_8 \cdot H_2O$

Fullers Earth

Colloidal Aluminum Silicate

VALFOR™ 150
(PQ Corp.
Valley Forge, Pa.)

$Na_2O \cdot Al_2O_3 \cdot (SiO_2)_x \cdot (H_2O)_y$

BENTONE™ 34, 38, SD-1, SD-2
(Rheox, Inc., Hightstown, NJ)

Organically modified
montmorillonite where
montmorillonite = $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$

Bentonites

$Al_2O_3 \cdot 4SiO_2 \cdot H_2O,$
 $R^{+}_{.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$

HECTALITE™ 200
(American Colloid Co.,
Arlington Heights, IL)

Smectite clay (Magnesium-
aluminum-silicate mineral)

ZEOSYL™ 110SD, DIAFIL™ 810
(J.M. Huber Corp., Borger, TX)

Hydrated amorphous SiO₂

HYDRITE™ R
(Dry Branch Kaolin Co.,
Dry Branch, GA)

Montmorillonites

Polyalkylene Oxide Polymers

TETRONIC™ 908, H-(OCH₂CH₂)_x-(OCHCH₂CH₂)_x- \ / (CH₂CH₂CHO)_x-CH₂CH₂O)-H
1508 NCH₂CH₂N
(BASF Corp.) H-(OCH₂CH₂)_x-(OCHCH₂CH₂)_x- / \ (CH₂CH₂CHO)_x-CH₂CH₂O)-H

POLYOX™ WSR N-10, WSR N-3000
WSR N-750
(Union Carbide Corp.
Danbury, Conn.)

(CH₂CH₂O)_n

CARBOWAX™ 400, 4600, 20M
(Union Carbide Chemicals
& Plastics)

HO-(CH₂CH₂O)_nH

Acrylic Polymers

CARBOPOL™ 907, 910
(The B.F. Goodrich Co.,
Akron, OH)

Acrylic acid, homopolymer
[(CH₂CHCOOH)_n]

CARBOPOL™ 614, 615
(The B.F. Goodrich Co.)

High MW Polyacrylic acid
crosslinked w/polyalkenylpolyether

CARBOPOL™ 613, 1622
(The B.F. Goodrich Co.)

Crosslinked acrylic copolymers

CARBOPOL™ 681 X-1
(The B.F. Goodrich Co.)

Acrylic polymer: ethyl
acrylate (formulated)

SOKALAN™ PA 70-PN, 110S
(BASF AG,
Ludwigshafen, Germany)

Linear Polyacrylic acid,
(MW: 70,000 & 250,000)

SOKALAN™ HP-22
(BASF AG)

CAS #25820-49-9 (copolymer)

COLLOID 117/50, 207

COLLOID X-0125-KN 706

SUBSTITUTE SHEET (RULE 26)

GOODRITETM K-7600 N (B.F. Goodrich Co.)	Linear polyacrylic acid, sodium salt (MW:60,000)
PARAGUMTM 511 (Para-Chem Southern, Inc. Simpsonville, S.C.)	
ALCOGUMTM L-11, L-15, L-27 L-37 (National Starch and Chemical Corp., Bridgewater, NJ)	Ethyl acrylate:methacrylic acid
ALCOGUMTM L-83 (National Starch and Chemical Corp.)	Ethyl acrylate:methyl methacrylate: methacrylic acid terpolymer
ACUSOLTM 842 (Rohm and Haas Co., Philadelphia, PA)	Ethyl acrylate:methacrylic acid
ACUMERTM 8100 (Rohm and Haas Co.)	
UCARTM 102, 104, 107 (Union Carbide Corp., Danbury, CT)	Dinonylphenoethoxylate/ TMN adduct, + ethyl acrylate, + methacrylic acid polymer (components)
UCARTM 146 (Union Carbide Corp.)	Butyl acrylate + styrene methacrylic acid polymer (components)
UCARTM 106 HE (Union Carbide Corp.)	Acrylic polymer - (trade secret)
TAMOLTM 731-D & 850 (Rohm and Haas Co.)	Acrylic acid polymer
MEROPANTM VD	Acetic acid ethenyl ester polymer with oxirane (C ₄ H ₆ O ₂ ·C ₂ H ₄ O) _x

Suitable cellulase enzymes for use in the novel stonewashing method include any cellulases, including those produced from fungal or bacterial sources that are optimally active in acidic solutions in degrading cellulosic fibers. Illustrative examples of such acid cellulase enzymes include CYTOLASETM and IndiAgeTM enzymes (produced by Genencor, Inc., South San Francisco, California) and CELLUSOFTTM and DENIMAXTM (produced by Novo Nordisk, Danbury, Conn.) which are derived from a strain of Trichoderma longibrachiatum (formerly T. reesei).

SUBSTITUTE SHEET (RULE 26)

It is to be understood, however, that the invention is not limited to any particular cellulase enzymes or any particular sources for such enzymes, but instead comprehends the use of any enzymes with cellulose degrading activity maximized in an acidic medium, which may be defined as a medium with a pH less than 7.0, but preferably within a pH range of about 4 to about 6.

To achieve the objects of the invention, it is necessary that the dye redeposition or backstaining inhibiting additives be present in the fabric treatment solution in a weight (w/w) concentration not less than about 0.005%. This minimum level may vary depending on the class of additives utilized. For example, the following are representative concentration ranges for the various classes of redeposition preventing additives, based on experimental test results:

Natural/synthetic inorganic silicates: .025 - 5.0%

Polyalkyleneoxide polymers: .025 - 2.5%

Polysaccharide polymers: .005 - 5.0%

Acrylic homopolymers and copolymers: .005 - 8.0%

It should be stressed that the above weight concentration ranges are based on the total weight of wash liquor in which the fabric is immersed and/or tumbled. The invention is not limited, however, to any specific method, sequence or formulation for adding the essential components of the invention, i.e. the acid cellulase enzymes and anti-redeposition additives to the wash liquor. For example, the enzymes and anti-redeposition additives can first be blended with suitable solvents and other optional ingredients, with the resultant formulation (in liquid, concentrate, gel or other form) being added to the wash water, or the individual components can be

separately added in dry or fluid form to the wash water.

The water-based compositions used in the novel method of the invention may include not merely appropriate weight concentrations of acid cellulase enzymes and anti-backstaining additives but also optional additional ingredients such as buffers to maintain the pH of the composition at a fairly stable level, surfactants to increase the wettability of the aqueous solution, promoting the activity of the enzyme in the treated fabric; solvents to help dissolve or disperse the enzymes and surfactants; cellulase activators; antioxidants; solubilizers; and builder components such as divalent sequestering agents. Representative examples of these optional ingredients include the following:

Surfactants - polyethylene oxide polymers, polypropylene oxide polymers, ethylene oxide-propylene oxide block copolymers, ethoxylated C₁₋₁₈ alkyl phenols and ethoxylated C₁₋₁₈ aliphatic alcohols.

Solvents - ethylene glycol, propylene glycol, and oligomers and higher polymers of ethylene or propylene glycol in the form of polyethylene or polypropylene glycols, alcohols, terpenes, and aliphatic, aromatic and naphthenic hydrocarbons.

Cellulase enzyme activators - proteins, cobalt and its salts, magnesium and its salts, calcium and its salts, potassium and its salts, sodium and its salts or monosaccharides such as mannose and xylose.

Antioxidants - tert-butylhydroxytoluene, 4,4'-butylidenebis(6-tert-butyl-3-methylphenol), 2,2'-butylidenebis(6-tert-butyl-4-methylphenol), monostyrenated cresol, distyrenated cresol, monostyrenated phenol, distyrenated phenol and 1,1-bis(4-

hydroxyphenyl)cyclohexane.

Solubilizers - lower alcohols such as ethanol, benzenesulfonate salts, lower alkylbenzenesulfonate salts such as p-toluenesulfonate salts, glycols such as propylene glycol, acetylbenzenesulfonate salts, acetamides, pyridinedicarboxylic acid amides, benzoate salts and urea.

Builders - organic phosphates, phosphonates, phosphonocarboxylates, amino-polyacetates, polyacrylic acids; non-dissociating polymers such as polyethylene glycol, polyvinyl alcohol and polyvinyl pyrrolidone, and salts of dicarboxylic, diglycolic and sulfonated carboxylic acids, borates, citrates and mixtures thereof.

The enzyme compositions used in the novel methods may be in any conventional form, including liquids, thickened liquids, concentrates, gels or solids. Various such compositions have been disclosed in the prior art and are known to those of skill in the formulation of textile treatment and processing products.

The following are representative examples of water-based compositions according to the present invention for use in the novel method of treating dyed fabric or garments to produce a stonewashed appearance while substantially preventing redeposition of dye onto the treated material. These examples are not intended, however, to limit the invention in any way or to set forth ingredients, materials or concentration ranges which must be used exclusively to practice the invention.

Examples 1-7 define compositions for use in the present invention which contain an acid cellulase enzyme derived from *T. longibrachiatum*, a buffer comprising 31.2% sodium acetate, 23.3%

acetic acid and 45.5% water, the specified dye redeposition preventing additive and water, quantity sufficient to 100% by weight.

EXAMPLE 1

		<u>%</u>
Enzyme	-	1.0
Buffer	-	2.0
BENTONITE™	-	0.1

EXAMPLE 2

Enzyme	-	0.125
Buffer	-	50.0
ZEOSYL™ 110 SD	-	0.5

EXAMPLE 3

Enzyme	-	0.25
Buffer	-	50.0
TETRONIC™ 908	-	0.5

EXAMPLE 4

Enzyme	-	0.75
Buffer	-	2.0
POLYOX™ WSRN-750	-	0.1

EXAMPLE 5

Enzyme	-	0.5
Buffer	-	0.5
POLYOX™ WSRN-3000	-	0.5

EXAMPLE 6

Enzyme	-	0.75
Buffer	-	2.0
CARBOPOL™ 910	-	0.1

EXAMPLE 7

Enzyme	-	0.5
Buffer	-	0.5
CARBOPOL™ 910	-	0.5

EXAMPLE 8

Laboratory testing was performed utilizing the compositions of Examples 1-7 in the wet processing of indigo dyed denim fabric to quantify the anti-backstaining benefit of each additive. The method used to determine changes in antibackstaining characteristics was to measure the Total Color Difference (ΔE) on a HunterLab 0/45 D25-PC2 Colorimeter, available from Hunter Associates Laboratory, Inc., Reston, VA. This instrument reads three opponent-color scales, where L represents black \rightarrow white (where black=0 and white=100), a represents red \rightarrow green (where +a = red, and -a = green), and b represents yellow \rightarrow blue (where +b = yellow, and -b = blue). ΔE is calculated by the following formula:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

Initial and final L,a,b readings are performed at the same location on individual test swatches.

Testing was performed in a Launder-Ometer, available from Atlas Electric Devices Co., Chicago, IL. The Launder-Ometer is an AATCC-approved standard laboratory washing machine which rotates (at 40 ± 2 rpm) up to 20 - 3 in. X 8 in. stainless steel cannisters (1.2 liter capacity) in a thermostatically controlled water bath. Each canister contained 200g. of one test solution of Examples 1-9, one - 4 in. X 4 in. white cotton swatch, one - 4 in. X 4 in. desized 14 oz. indigo denim swatch, and 45 - .25 in. stainless steel balls.

The pH of each test solution was adjusted to 5.0 ± 0.1 units. Each canister was sealed and rotated in the Launder-Ometer at $132 \pm 2^\circ\text{F}$ for 60 or 75 minutes. At the conclusion of the test, the fabric swatches were removed and rinsed in a

Kenmore (Series 60) home washer at a low water level for a six minute cycle. At the completion of the spin cycle, all test swatches were dried in a conventional domestic dryer. Final L,A,b readings were taken and the Total Color Difference (ΔE) was calculated for the white test swatches. Percent improvement (%I) in ΔE for each test solution in comparison with control solution (the same concentrations of enzyme and buffer without the antibackstaining additives) was calculated as follows:

$$\%I = \left(1 - \frac{\Delta E_{\text{test}}}{\Delta E_{\text{control}}} \right) \times 100$$

Using the above described test method, Table A lists percentage improvement values for the various backstaining inhibiting additives used in Examples 1-7.

TABLE A

<u>Test Solution</u>	<u>Time (min.)</u>	<u>%I</u>
Ex. 1	60	21
Ex. 2	60	23
Ex. 3	75	15
Ex. 4	60	24
Ex. 5	75	23
Ex. 6	60	33
Ex. 7	75	69

EXAMPLE 9

Twenty four pounds (24 lb.) of previously desized denim jeans plus a white cotton test swatch were placed in a 125 lb. capacity Milnor open-pocket washer-extractor. The machine was filled with 35 gallons of water and heated to 138°F (59°C). The specified antibackstaining additive and 21.7 ml. of acid cellulase enzyme per kg. of denim were then added to the washer and tumbled for twenty five minutes. An acetate buffer was also included to control the pH at 5.1 ± 0.1 units. The wash liquor was dumped and the contents of the washer were rinsed at 140°F (60°C) then 110°F (43°C) in 37 gallons of water. The garments and test swatches were then dried and final L,a,b readings were taken. Table B indicates the additive doses and the respective ΔE values.

TABLE B

<u>Additive</u>	<u>Dose</u>	<u>ΔE</u>
(gm. additive/kg. denim)		
None - Control	-	34.8
Xanthan Gum	10.61	24.5 (%I=29.6)
Sodium Alginate	10.45	24.8 (%I=28.7)

EXAMPLE 10

Twenty one pounds (21 lb.) of denim jeans plus a white cotton test swatch were placed in an 85 lb. capacity Unimac open-pocket washer-extractor. The machine was filled with 38 gallons of 140°F (60°C) water containing an amylase enzyme desizing stripper. After 12 minutes, the desizing solution was drained.

The machine was filled with 42 gallons of 120°F (49°C) water for a 2 minute rinse. The washer was again filled with 42 gallons of 140°F (60°C) water. The antibackstaining additive and 18.6 ml. of acid cellulase enzyme per kg. of denim were then added to the washer and tumbled for twenty minutes. An acetate buffer was also included to control the pH to 5.1. The wash liquor was then dumped and the contents of the washer were rinsed three successive times at 120°F (49°C) in 68 gallons of water. The garments and test swatches were then dried and final L,a,b reading were taken. Table C indicates the additive doses and the respective ΔE values.

TABLE C

<u>Additive</u>	<u>Dose</u>	<u>ΔE</u>
(gm. additive/kg. denim)		
None - Control	-	29.9
Ethylacrylate: methacrylic acid copolymer	3.57	22.1 (%I=26.1)

It has thus been shown that there are provided methods which achieve the various objects of the invention and which are well adapted to meet the conditions of practical use.

As various possible embodiments might be made of the above invention, and as various changes might be made in the embodiments set forth above, it is to be understood that all matters herein described are to be interpreted as illustrative and not in a limiting sense.

What is claimed as new and desired to be protected by Letters Patent is set forth in the following claims.

1. A method of treating dyed cellulosic fabric, in unsewn form or in the form of a garment or other article composed of sewn fabric, to produce a stonewashed effect in said fabric comprising contacting said fabric with a water-based composition having an acidic pH and including (a) at least one cellulase enzyme having optimum cellulose degrading activity in an acidic medium and (b) a dye redeposition inhibiting additive selected from the group consisting of natural and synthetic inorganic silicates, polyalkylene oxide polymers, acrylic polymers, and natural, synthetic and semisynthetic polysaccharides.

2. A method according to claim 1 wherein said composition comprises from about .025 to about 5.0% by weight of natural or synthetic inorganic silicates.

3. A method according to claim 2 wherein said inorganic silicates are selected from the group consisting of kaolin clays, fullers earth, zeolites, bentonites, smectite clays and hydrated amorphous silicon dioxide.

4. A method according to claim 1 wherein said composition comprises from about .025 to about 2.5% by weight of polyalkylene oxide polymers.

5. A method according to claim 4 wherein said polyalkylene oxide polymers are selected from the group consisting of polyalkylene oxide polyamine copolymers, polyethylene oxides and polyethylene glycols.

6. A method according to claim 1 wherein said composition comprises from about .005 to about 5.0 % by weight of acrylic polymers.

7. A method according to claim 6 wherein said acrylic polymers are selected from the group consisting of homopolymers

of acrylic acid or methacrylic acid and copolymers of said acids with esters of said acids, polyalkenyl polyether or styrene.

8. A method according to claim 1 wherein said composition comprises from about .005 to about 8.0% by weight of natural, synthetic or semisynthetic polysaccharides.

9. A method according to claim 8 wherein said natural, synthetic or semisynthetic polysaccharides are selected from the group consisting of natural and synthetic gums and thickeners, hydroxylated cellulose materials, gelatin and casein.

10. A method according to claim 9 wherein said gums are selected from the group consisting of xanthan, rhamosan, welan, guar and locust bean gums.

11. A method according to claim 9 wherein said thickeners are selected from the group consisting of alginic acid, sodium alginate and other alginic acid metallic salts.

12. A method according to claim 9 wherein said cellulosic materials are selected from the group consisting of hydroxyethylcellulose, hydroxypropylmethylcellulose and hydroxybutylmethylcellulose.

13. A method according to claim 1 wherein said composition has a pH of about 4 to 6.

14. A method according to claim 1 wherein said enzyme is derived from a strain of Trichoderma longibrachiatum.

15. A method according to claim 1 wherein said composition additionally includes a buffer.

16. A method according to claim 1 wherein said composition additionally includes surfactants, solvents, enzyme activators, antioxidants, solubilizers or builders.

17. A method according to claim 1 wherein said fabric

is tumbled or agitated with said composition.

18. A method according to claim 17 wherein said fabric is tumbled or agitated in a washing machine, tumbler, converted dryer or dye paddle machine.

19. A method according to claim 1 wherein said fabric is in unsewn form.

20. A method according to claim 1 wherein said fabric is in the form of a garment.

21. A method according to claim 20 wherein said garment is a new garment.

22. A method according to claim 1 wherein said fabric is dyed with a vat dye, a pigment dye, a sulfur dye, or other dye wherein the dye resides primarily on the surface of the fibers of the fabric.

23. A method according to claim 22 wherein said fabric is dyed with indigo dye.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 95/06578

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/386 D06P5/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D D06P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,91 19794 (NOVO NORDISK AS) 26 December 1991 see page 5; claims; example 2	1,4,5, 13,15-23
X	WO,A,93 25655 (GENENCOR INT) 23 December 1993 see page 23; examples see page 14	1,5,13, 15-23
X	WO,A,90 02790 (ECOLAB INC) 22 March 1990 cited in the application see page 14; claims; tables 4-8	1-12, 15-23
A	WO,A,94 07983 (GENENCOR INT) 14 April 1994 see page 55; examples 18,19	1,14

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

20 September 1995

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INTERNATIONAL SEARCH REPORT

Internet Application No
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